Direct determination of epitaxial interface structure in Gd_2O_3 passivation of GaAs

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Obtaining accurate structural information on epitaxial films and interfaces is nowhere more critical than in semiconductor passivation layers, where details of the atomic structure and bonding determine the nature of the interface electronic states. Various non-destructive methods have been used to investigate the structure of films and interfaces[1–6], but their interpretation is model-dependent, leading occasionally to wrong conclusions. We have developed a new X-ray method for the direct determination of epitaxial structures, coherent Bragg rod analysis (COBRA). The usefulness of our technique is demonstrated by mapping, with atomic precision, the structure of the interfacial region of a Gd_2O_3 film grown epitaxially on a (100) GaAs substrate. Our findings reveal interesting behaviour not previously suggested by existing structural methods, in particular a lock-in of the in-plane Gd atomic positions to those of the Ga/As atoms of the substrate. Moreover, we find that the bulk stacking of the Gd_2O_3 atomic layers is abandoned in favour of a new structure that is directly correlated with the stacking sequence of the substrate. These results have important implications for Gd_2O_3 as an effective passivation layer for GaAs (ref. 7). Our work shows that the COBRA technique, taking advantage of the brilliance of insertion device synchrotron X-ray sources, is widely applicable to epitaxial films and interfaces.

A solution to the phase problem in the context of two-dimensional (2D) structures such as films and interfaces has been elusive. Previous attempts have been limited to the determination of layer electron densities[8] or have led to recursion formulae[9,10], which are cumbersome, slow to converge and essentially limited to simple structures.

In this work, carried out at the Michigan-Howard-Lucent Technologies (MHATT) and Pacific Northwest Consortium (PNC) undulator beam lines at the advanced photon source (APS), we demonstrate a solution to the problem of determining the structure of thin films and their interface with the substrate, making use of the high brilliance characteristics of the APS undulator radiation. The method is general, and can be applied to any epitaxially grown structure.

The COBRA experiments were performed on a thin (2.7 nm) epitaxial layer of Gd_2O_3 deposited by molecular beam epitaxy (MBE) on a (100) GaAs wafer[11]. The X-ray scattering from such a system is composed of sharp Bragg peaks from the 3D-ordered GaAs substrate, together with continuous scattered intensity along lines in reciprocal space (Bragg rods) associated with the 2D periodic regions (the substrate truncation, the interface, and the Gd_2O_3 film itself). The intensity profile along the Bragg rods is a coherent combination of all these contributions; namely, it is proportional to the absolute value squared of the sum of the corresponding complex scattering factors (CSFs).

The in-plane symmetry consists of two mirror planes[11]. We have measured the diffraction intensities along 13 Bragg rods that were not symmetrically equivalent and used symmetry to obtain all other rods. We have also measured two symmetry-related rods and confirmed that, within experimental accuracy, the symmetry-related rods are equal. We then used COBRA to determine the CSFs along the rods and to obtain the corresponding electron density of the epilayer/substrate system by Fourier transforming the CSFs into real space.

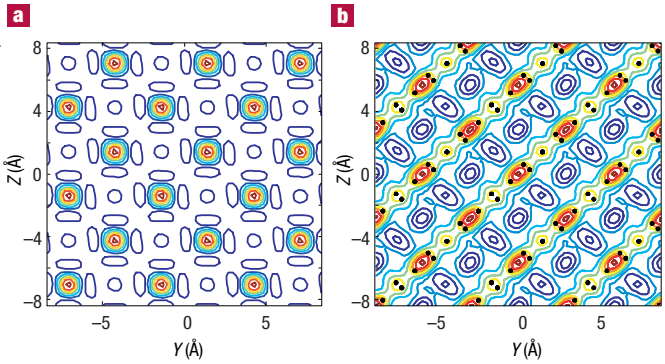

Figure 1 COBRA electron-density maps of Gd_2O_3–GaAs (100) epitaxial structure. Low density, cold colours; high density, warm colours. **a**, Eighth Ga/As monolayer below the nominal interface; **b**, Ninth Gd_2O_3 layer above the interface. The black dots are the folded bulk in-plane Gd positions (see text). *Y* and *Z* denote the position within a particular plane parallel to the interface.

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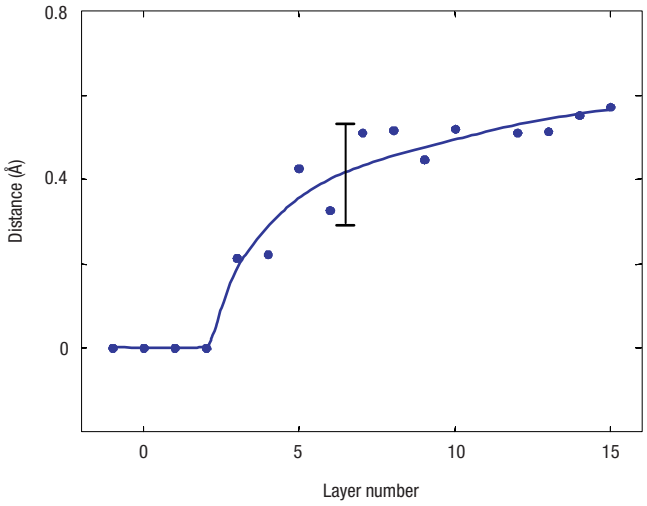

Figure 2 The distance between the in-plane Gd position and the nearest large electron-density peak as a function of the layer number. The error bar indicates the maximum uncertainty.

In our case we consider the CSF to be a coherent sum of contributions from a reference structure (substrate plus a film with the Gd_2O_3 bulk structure) and an unknown electron density that, when added to the reference electron density, yields the actual electron-density distribution of the whole system. A detailed discussion of the method has been given elsewhere[12]. Briefly, we make use of the fact that the CSFs vary continuously along the Bragg rods. Because the reference contains some information on the film structure, and the film and substrate are spatially separated, we can, by appropriate choice of the real-space coordinate system, make the CSF of the reference structure vary rapidly along the Bragg rods compared with that of the unknown part. In this case, the CSFs of the unknown part at any two adjacent points along the Bragg rod are roughly equal. This allows us to calculate the unknown CSF from the measured diffraction intensities and the known CSFs of the reference at these two points. We have calculated in this way the amplitude and phase of the CSFs on all 13 Bragg rods and then Fourier transformed them into real space to obtain the structure's 3D electron density. To check the consistency of this electron density with experiment, we compared the diffraction intensity profiles it would produce with the experimentally measured ones on all 13 Bragg rods. The agreement we obtained was excellent.

Previous work on the Gd_2O_3–GaAs interface[13–15] has shown, among other things, that the Gd_2O_3 film grows as a single-domain crystal with three Gd_2O_3 unit cell edges roughly commensurate with four GaAs diagonals and one Gd_2O_3 face diagonal matching two GaAs face diagonals. Because the periodicity of the Gd_2O_3 structure is a multiple of that of GaAs, the CSF function along the GaAs-defined Bragg rods is the Fourier transform of the electron density folded into a GaAs-defined 2D unit cell[12]. The 'folded structure' here is obtained by translating each atom into the 2D unit cell using the GaAs in-plane unit cell vectors. An example of the folded structure is shown in Fig. 1. The black dots on Fig. 1b are the folded positions of the Gd atoms in one layer of the bulk Gd_2O_3 structure, projected onto the substrate plane. The oxygen atoms are not considered because they are weakly scattering compared with Gd. Each dot of a pair represents two folded atoms and each single dot represents four folded atoms at slightly different heights. Notice that the folded positions form lines. One therefore expects that the electron-density function will have ridges along these lines separated by valleys.

The electron-density function contains a great deal of quantitative structural information such as atomic positions in each layer, and surface or interface roughness, as well as strain-induced disorder. Samples with film thickness similar to that reported here (~2.7 nm) have been found to be essentially free from misfit dislocation defects[11]. Therefore we do not expect, or indeed observe, significant interface disorder in such thin films. Here we focus on two particularly surprising results, namely the displacement of the Gd atoms in the first few Gd_2O_3 layers as they lock in to the substrate Ga/As positions, and the appearance of a stacking arrangement of the epitaxial film which conforms to that of the substrate rather than that of bulk Gd_2O_3.

Two examples of the electron-density maps obtained by COBRA are shown in Fig. 1. Each map consists of 3 × 3 GaAs 2D unit cells. Figure 1a is the eighth layer below the interface on the GaAs side and Fig. 1b is the ninth layer above the interface on the Gd_2O_3 side. The first map clearly shows the Ga or As atomic positions. The second shows the ridges and valleys expected from the folded structure. The small peaks along each ridge coincide with a single black dot, or a pair of black dots, which, as described above, represent four folded Gd atoms each. However, the other dots do not coincide with peaks in the electron-density map. Instead we have a large peak between the dots. This means that these folded atoms are displaced from their corresponding bulk positions. We have analysed the electron density along the ridges to determine the distance of the folded atom positions from the peak positions and found that the distance varies with layer number as shown in Fig. 2. This result shows that the positions of the folded Gd atoms in the first few layers coincide with the peak positions. Further away from the interface their positions relax to the positions expected in bulk Gd_2O_3.

From the relation between the electron-density peak positions and the folded Gd positions we can now infer the Gd positions in the real unfolded structure. In Fig. 3 we show four consecutive layers. The Gd atoms in rows 1, 2, 4 and 5 fold to the positions on both sides of a large peak in the electron-density map, whereas the atoms on rows 3 and 6 fold to the positions that coincide with the small peaks. In the first few layers, the Gd atoms in rows 1, 2, 4 and 5 are locked to the underlying Ga and As positions (circles) whereas further away from the interface they relax to the bulk Gd_2O_3 positions (Fig. 2).

An even more striking result is the stacking order. Note that in Fig. 3 the Gd positions in one layer can be located by displacing the atoms in the

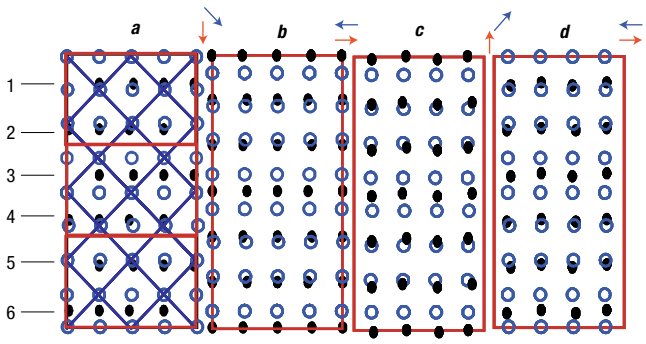

Figure 3 In-plane Gd positions (dots) in four consecutive layers of the Gd_2O_3 film. Each large rectangle represents one 2D super-cell composed of 3 Gd_2O_3 cells (red) and 16 GaAs cells (blue). The positions of the substrate Ga/As atoms (circles) in four consecutive layers are shown superimposed. The layer sequence *a*, *b*, *c*, *d* repeats throughout the sample. Note that the Gd atoms and the Ga/As positions shift in roughly the same way (denoted by the lower line of (red) vectors) from one layer to the next, and are quite different from the corresponding in-plane position shifts in bulk Gd_2O_3, denoted by the upper line of (blue) vectors.

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previous layer by the red (lower line) vector shown between the two. In contrast it turns out that in bulk Gd_2O_3 the layers are related by the blue (upper line) vectors, meaning that the stacking orders in the film and in the bulk are different. What is really surprising is that the displacements of the Gd atoms and those of the Ga and As atoms in every four consecutive layers are the same: the Gd atoms abandon the stacking order of bulk Gd_2O_3 in favour of the stacking order in GaAs. This tendency to conform to the underlying substrate provides insight into why Gd_2O_3 is an effective passivation layer for GaAs and why it allows field-effect transistors to be made on GaAs (ref. 15).

Our work demonstrates that the COBRA method can determine the 3D electron density of an epitaxial interface and film with sub-angstrom resolution. In the present case, the results are even qualitatively different from the bulk Gd_2O_3 structure, suggesting that fitting methods starting with such a model will lead to wrong conclusions. The folded electron-density function that COBRA provides contains much more structural information than that provided by local probe methods such as XAFS[14]and X-ray holography[16] because these average over a large number of probe inequivalent positions. Moreover, our new technique is non-invasive and the electron-density function it provides can be compared with theoretical models. The method is general, and the fact that the computation time scales linearly with the number of atoms, rather than geometrically as in a conventional full-matrix intensity refinement procedure[17], means that it can be used on systems with very large 2D unit cells. For example, we analysed the simulated diffraction data of an organic molecule with about 1,000 atoms arranged in a 2D array on a molecular crystal, and were able to reconstruct its structure faithfully. The method provides a highly efficient procedure for directly extracting real-space structures from Bragg rod measurements on a wide variety of epitaxial materials.

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References

1. Robinson, I. K. & Tweet, D. J. Surface x-ray diffraction. *Rep. Prog. Phys.* **55,** 599–651 (1992).
2. Miceli, P. F., Palmstrom, C. J. & Moyers, K. W. Growth morphology of epitaxial ErAs/GaAs by x-ray extended range specular reflectivity. *Appl. Phys. Lett.* **61,** 2060–2062 (1992).
3. Zegenhagen, J. Surface-structure determination with x-ray standing waves. *Surf. Sci. Rep.* **18,** 199–271 (1993).
4. Sinha, S. K. X-ray Diffuse-scattering as a probe for thin-film and interface structure. *J. Physique III* 1543–1557 (1994).
5. Robinson, I. K. Crystal truncation rods and surface-roughness. *Phys. Rev. B* **33,** 3830–3836 (1986).
6. Stern, E. A. & Heald, S. M. in *Handbook on Synchrotron Radiation* Vol. 1B (eds Koch, E.-E., Eastman, D. E. & Farge, Y.) 955–1014 (North Holland, Amsterdam, 1983).
7. Hong, M. *et al.* Epitaxial cubic gadolinium oxide as a dielectric for gallium arsenide passivation. *Science* **283,** 1897–1900 (1999).
8. Sanyal, M. K. *et al.* Fourier reconstruction of density profiles of thin films using anomalous X-ray reflectivity. *Europhys. Lett.* **21,** 691–696 (1993).
9. Torrelles, X., Rius, J., Miravitlles, C. & Ferrer, S. Application of the 'direct methods' difference sum function to the solution of reconstructed surfaces. *Surf. Sci.* **423,** 338–345 (1999).
10. Saldin, D. K., Harder, R., Vogler, H., Moritz, W. & Robinson, I. K. Solving the structure completion problem in surface crystallography. *Comput. Phys. Commun.* **137,** 12–24 (2001).
11. Kortan, A. R., Hong, M., Kwo, J., Mannaerts, J. P. & Kopylov, N. Structure of epitaxial Gd_2O_3 films grown on GaAs (100). *Phys. Rev. B* **60,** 10913–10918 (1999).
12. Yacoby, Y. *et al.* Direct structure determination of systems with two-dimensional periodicity. *J. Phys.: Condens. Matter* **12,** 3929–3938 (2000).
13. Bolliger, B. *et al.* Structure of epitaxial Gd_2O_3 films and their registry on GaAs (100) substrates. *Surf. Interface Anal.* **30,** 514–17 (2000).
14. Nelson, E. J., Woicik, J. C., Hong, M., Kwo, J. & Mannaerts, J. P. Extended X-ray absorption fine-structure measurement of bond-length strain in epitaxial Gd_2O_3 on GaAs(001). *Appl. Phys. Lett.* **76,** 2526–2528 (2000).
15. Hong, M. *et al.* Initial growth of $Ga_2O_3/(Gd_2O_3)$ on GaAs: key to the attainment of a low interfacial density of states. *Appl. Phys. Lett.* **76,** 312–314 (2000).
16. Tegze, M. & Faigel, G. X-ray holography with atomic resolution. *Nature* **380,** 49–51 (1996).
17. Uson, I. & Sheldrick, G. M. Advances in Direct Methods for Protein Crystallography. *Curr. Opin. Struct. Biol.* **9,** 643–648 (1999).

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Competing financial interests

The authors declare that they have no competing financial interests.

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